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Relation between vapour pressure and internal pressure in liquids

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From statistical thermodynamical considerations the relation $p = p_c \exp(-\pi_i V/2RT)$ is derived, where p_c is the vapour pressure of the liquid, p_c the critical pressure, π_i the internal pressure and V the molar volume. The relation is tested for thirty liquids—polar and non-polar—by examining the slope of the $\ln(p_c/p)$ versus $\pi_i V/T$ graph and comparing it with the value of the universal gas constant, using experimentally available data for the computation of the internal pressure.

1. INTRODUCTION

Recently one of us pointed out the nature of internal pressure and its thermodynamic significance in transport processes. (Suryanala-yana 1972, 1973). In this paper a quantitative relation is sought between the internal pressure of a liquid and its vapour pressure. Viewed as a rate process, vapourisation requires the liquid molecule to cross and energy barrier which accounts for cohesion in liquids. This justifies a possible existence of a quantitative relationship.

2, THE DERIVATION

From the work of Glasstone, Laider and Eyring (1941) it is clear that vapourisation involves transport of the molecule through the liquid surface barrier. For our purpose we make use of the concept that the configuration corresponding to the activated state has all the properties of an ordinary molecule except for one normal vibration frequency which has an imaginary value. If the top of the energy barrier where the activated complex is situated is relatively flat, this motion along the reaction path may be treated statistidallyas a one dimensional translation. It is reasonable to assume the acivated complexes as being always in equilibrium with the reactants. Hence it should be possible to apply the methods of statistical mechanics to the constituents of the reaction.

At equilibrium, the chemical potential of the species in the two phases will be equal. The molar free energy G is related in general to the partition function Q by the relation.

$$G = -kT \ln Q + PV \tag{1}$$

The partition function Q_1 of a gram.mole of the liquid is

$$Q_1 = \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V_f b_1 e^{-E_0/RT} \right] \tag{2}$$

where, N is Avagadro's number, V_f the free volume and b_1 the contribution to the partition function due to causes other than translation (Eyring, 1936; Glasstone & Tayloe 1951; Rowlisonn, 1969), each molecule being assumed to be confined within the unit cell ((Peak & Hill 1950). For easy handling we denote the translation parameter $(2\pi mkT/h^2)^{3/2}$ by T_p.

In general, after Eyring and Walter (1941) the partition function of the liquid phase is considered to be made up of a combination of the partition function of the liquid molecules and of the holes in suitable proportion. Thus seen E_0 represents the average potential energy (per mole) of the molecules in their equilibrium positions, if they are assumed for a moment to be in the solid state. What is really important is that the difference between the potential energy of the liquid state (u_l) and that in the gaseous state ($u_g = 0$) is E_0 and is therefore a negative quantity. As such $\exp(-E_0/RT)$ should be replaced by $\exp(\lambda_0/RT)$ wherein λ_0 is the molar energy of vapourisation. In the present case of the passage of the vapourisation. In the present case of the passage of the liquid molecules across the energy barrier, the energy of vapourisation required is equal to half the nergy of all the bonds a molecule forms in the liquid (i.e.) half the cohesive energy which is equal to $(\pi_i V/2)$ (Henry, 1971; Henry & John 1969).

Here π_i is the internal pressure of the liquid and V, the molar volume, therefore

$$\lambda_0 = \frac{\pi_i V}{2} \qquad \ldots (3)$$

The molar free energy of the liquid is therefore,

$$G_1 = -kT \ln Q_1 + PV_1 \qquad \ldots (4)$$

$$= -kT \ln \left[T_p V_f b_1 \exp \left(\frac{\pi_i V}{2RT} \right) \right] + PV_1 \qquad \ldots (5)$$

$$= -NkT \ln (T_p V_f b_l e^{\pi_i V/RT}) + PV_1 \qquad \ldots (6)$$

v_1 being too small $PV_1 << NkT$ and hence is negligible. We may remember $Nk = R$ and write $G_1 = -RT \ln (T_p V_f b_l) - \frac{\pi_i V}{2}$ ... (7)

data for as many as 30 liquids. For computing the intrnal pressure, we have $\pi_i = (\partial E/\partial V)$ by definition from which, the follcwing relations are obtained :

$$(\pi_i + p') = \frac{\Delta E_{vap}}{V} \qquad \ldots \quad (18)$$

$$(\pi_i + p') = \frac{T\alpha}{\beta_T} \qquad \ldots \quad (19a)$$

Eq. (19a) is straightaway a thermodynamic equation. In eqs (18), (19a) and in the following (19b) and 19c), T is the absolute temperature, α, the thermal volume expansivity, β_T the isothermal compressibility, u, the adiabatic ultrasonic velocity, ρ, the density, γ, the ratio of specific heats, C_p, the molar heat capacity at constant pressure, J, the mechanical equivalent of heat, $(\Delta E)_{vap}$, the molar heat of vapourisation and V, the molar volume. By substituting $\beta_T = \gamma\beta_s$ and equating $\beta_s = 1/u^2\rho$ we get the relation

$$(\pi_i + p') = \frac{T\alpha u^2\rho}{\gamma} \qquad .. \quad (19b)$$

Making use of the thermodynamic relationship,

$$C_p - C_v = -\frac{\alpha^2 T V}{\beta}$$

we get

$$(\pi + p') = \left(\frac{T\alpha C_p J u^2\rho}{C_p J + u^2\alpha^2 T}\right) \qquad \ldots \quad (19c)$$

One or the other of the above expressions has been used depending on the availability of the experimental data to compute π_i. Table gives the data and column 6 the particular relation used for each liquid.

The value of the internal pressure (π) is usually of the order of theousands of atmospheres and hence P' in eq. (18) and (19), which is 1 atmosphere, can be neglected. The sources of data for the computation for the various liquids are given in column 7 under reference in table. In the computation, the variation of acoustic velocity with frequency (if any) is neglected and the liquids are assumed to have no acoustic dispersion. The ratio of specific hezts (γ) of the liquids is assumed to remain constant at all temperatures.

A graph plotting $\ln(p_c/p)$ vs $(\pi_i V/T)$ should be linear and the reciprocal of its slope, we set $2R[JK^{-1}$ mole$^{-1}]$ According to eq. (15), half of the reciprocal of the slope $2R$ must be equal to R, the gas constant.

Table 1

Liquids (classified			Temperature			Value of R (J.K.$^{-1}$mp.$^{-1}$)	Formula for π	References
			Range °K	No. of temperature	Interval			
Non-polar organc substances	Aromatics	Benzene	278–353	10	10°K (mostlu)	9.41	19–c	16, 17
		Toluene	293–323	4	10°K	9.315	19–b	18, 19, 20
		m. Xylene	273–323	6	10°K	8.635	19–b	18, 19, 20, 21 22
	Aliphatics	Methane	95–110	4	5°K	8.75	18	23, 24
		Propane	143-228	10	10°K	9.915	19–a	21, 25
		n. Butane	183-268	10	10°K	9.445	19–a	17, 25
		n. Pentane	243–303	7	10°K	10.23	19–b	18, 19, 26, 27
		n. Hexane	273–313	5	10°K	9.85	19–b	17, 18, 20
		Cyclohexane	303–343	5	10°K	10.315	19–b	19, 20, 22
		Carbon Tetrachloride	298–313	4	5°K	10	19–b	18, 20, 30, 31
		Triethylamine	273–323	6	10°K	10.185	19–c	16, 17
		Carbon-disulphide	4	4	10°K	7.855	19–b	18, 19, 20
Polar substances	Substances with H-bonds (in order of descending concentration of H-bonds (energy)	Water	273–373	7	20°K	8.462	18	38, 39
		Methyl alcohol	283–313	4	10°K	2.965	19–b	19, 20, 22
		Ethyl Alcohol	283–313	4	10°K	5.5	19–b	18, 19, 20
		n-Propyl alcoho.	273-313	5	10°K	4.85	19–b	17, 20, 28
		i-Propyl alcohol	273–313	5	10°K	5.25	19–b	17, 19, 20
		n-Butyl Alcohol	273–313	5	10°K	6.15	19–b	17, 19, 20, 21
		i-Butyl Alcohol	273–313	5	10°K	5.375	19–b	17, 19, 20, 21
		Chloroform	273–313	3	10°K	6.75	19–a	32
		Aniline	283–323	5	10°K	7.425	19–b	18, 19, 20
		Hydrogen Bromide	191–206.4	4	5°K	7.915	19–a	29
	Polar substances	Acetone	273–323	6	10°K	7.425	19–b	18, 19, 29
		Ethyl Bromide	273–303	4	10°K	8.215	19–a	19, 21, 33
		Methyl Acetate	283–323	5	10°K	9.755	19–b	18, 19, 20, 29
		Ethyl Acetate	283–323	5	10°K	10.375	19–b	18, 19, 20, 29
		Ethyl Formate	283–323	5	10°K	10.4	19–b	17, 19, 20
		Argon (liquid)	83.81–87.29	3	—	7.72	19–a	34
		Nitrogen (liquid)	65–75	3	5°K	7.49	19–a	35
		Oxygen (liquid)	65–90	6	5°K	8.235	18	26, 37

*Substances with strong specific intermolecular forces (H-bonds, multi-poles)

Figures (1) to (6) represent the variation of $(\pi_i V/T)$ with ln (p_c/p). It is obvious as a first step that the plot of $\ln(p_c/p)$ *vs* $(\pi_i V/T)$ is nearly linear. Except for water, *n*-heptane and a few other cases the lines pass through the origin as

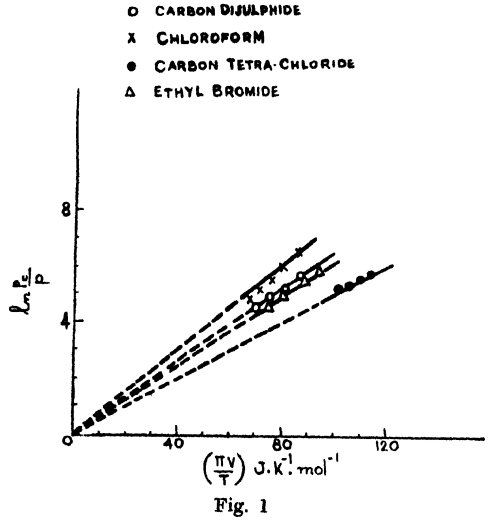


Fig. 1

postulated by eq. (15). Column 5 of the Table gives the values of $R[JK^{-1}\text{ mole}^{-1}]$ obtained for different liquids classified under the headings of non-polar[2] and polar

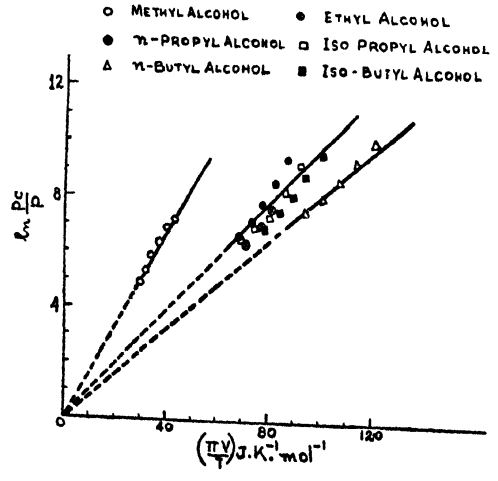


Fig. 2

organic liquids. The value of $R[JK^{-1}\text{ mole}^{-1}]$, if it were equal to the gas constant R should be $8.3166 \pm 0.0004 J.K.^{-1}\text{mol.}^{-1}$. As can be seen in column 5 of the

Table , R scatters around this value. In non-poar solvents the values of R are in general higher than R. In strongly polar organic substances such as acetone ($\mu = 2.75$), ethyl bromide and especially substances having hydrogen bonds,

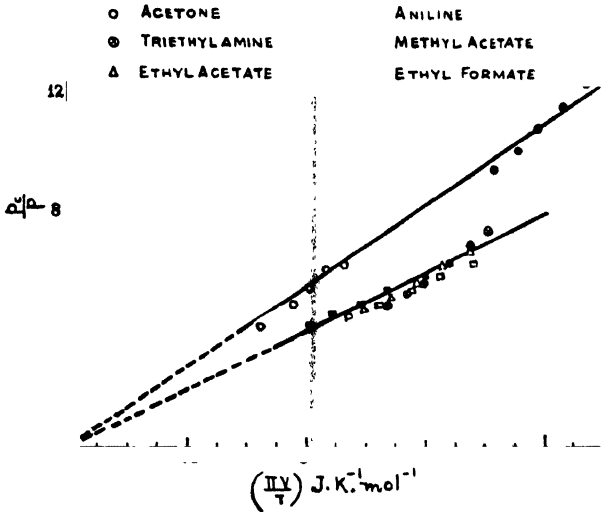
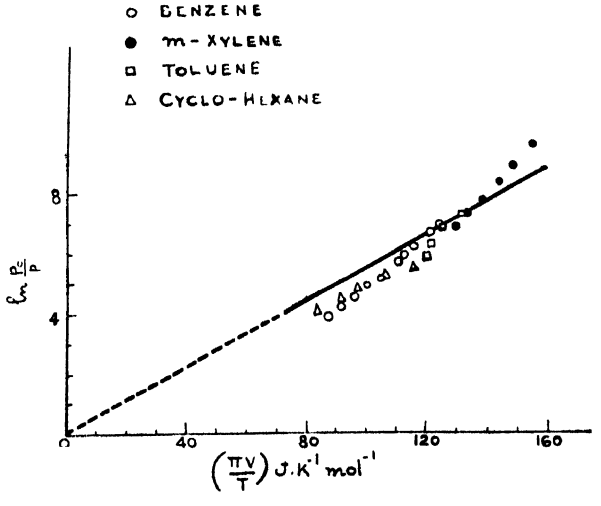


Fig. 3

the R-values are smaller than the gas constant R. The deviation from R is rising with the concentration of the H-bond energy : the lowest R-value we note for methyl alcohol, having the greatest concentration of H-bond energy in the series



Fig, 4

of alcohols. Peculiarly in the case of water, where the concentration of H-bond energy is extreme, the value of R is nearest to the gas constant.

In view of the different formulae used for the calculation of the internal pressure and the different degree of reliability of the data obtained from literaoure, we may summarise the experimental compliance as follows :

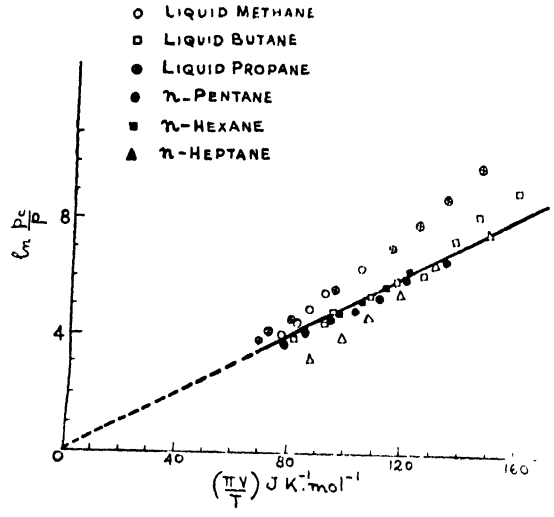


Fig. 5

1. For 15 liquids, the value of R is between 7.1 and 9.5 $J.K.^{-1}$ mole.$^{-1}$, that is with $\pm 15\%$ of the expected value Saha & Srivastava, 1965) (8.3166$\pm$0.0004) J.K.$^{-1}$.mol.$^{-1}$.

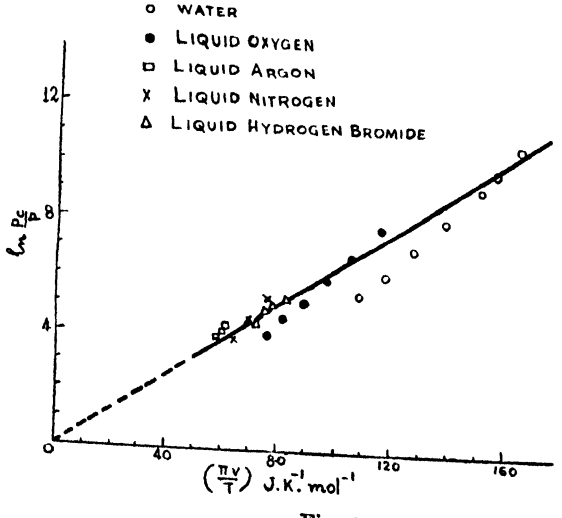


Fig. 6

2. For 5 liquids, the deviation from the expected value is within $\pm$ 2.08 .
3. For the alcohols in general, the value of R lies between 2.92 and 6.15 $J.K.^{-1}$.mol.$^{-1}$.

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